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Ab initio investigations of threshold displacement energies and stability of associated defects in cubic silicon carbide

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Abstract. Using first principles molecular dynamics simulations, we have recently determined the threshold displacement energies and the associated created defects in cubic silicon carbide. Contrary to previous studies using classical molecular dynamics, we found values close to the experimental consensus, and also created defects in good agreement with recent works on interstitials stability in silicon carbide. We have also investigated the stability of several Frenkel pairs, using transition state theory and constrained path calculations.

Introduction

The silicon carbide is a promising material with potential applications in electronics, as a replacement for silicon, and in nuclear technology. The properties of ion implanted silicon carbide have been largely investigated in recent years [1, 2]. Ion implantation leads to the creation of atomic-scale defects and local disorder in the crystal structure. In turn, defects accumulation can lead to the degradation of the electrical properties activated by implanted dopants. Moreover, microstructural changes, induced by irradiation, affect all properties of SiC-based devices and nuclear components. For this reason, irradiation-induced damage must be cured by a subsequent thermal annealing before the implants are rendered electrically active. A fundamental understanding of the accumulation and recovery of irradiation-induced defects is, then, essential to improve SiC-based technology.

A key quantity of the irradiation process, required as input in large-scale irradiation simulation packages, is the threshold displacement energy E_d. It may be defined as the minimal kinetic energy that has to be transferred to a lattice atom in order to create a stable Frenkel pair. This quantity is rather difficult to measure, since single created defects have to be identified during experiments, and associated with a well-defined irradiation energy. In silicon carbide, there have been several measurements, with different techniques, but a large dispersion of values is obtained [3]. It is usually assumed that average values for C and Si sublattices are 20 eV and 35 eV, respectively. There has been an increasing number of works aiming at determining E_d from molecular dynamics simulations. But, average values were found from 17 to 40 eV for C sublattice and from 42 to 57 eV for Si sublattice, with very different extreme values [4-9]. In addition, the nature of created defects is often different from one study to another. We have recently shown that these discrepancies are due to the use of different empirical potentials [10]. Indeed, the creation of a Frenkel pair is related to the energy barrier that the lattice atom must overcome to reach an interstitial site. Empirical potentials usually give a poor description of these saddle states, especially for covalent materials.

The recovery of irradiation-induced defects depends on their stability. Experimentally, the recovery of irradiation-induced defects is observed during thermal annealing experiments on 6H-SiC [11, 12]. Also, classical molecular dynamics calculations have already been performed for investigating the Frenkel pairs recombination in cubic silicon carbide [13]. However, since calculated displacement energies clearly depend on empirical potentials used [10], it would be worth to study Frenkel pairs stability with the first principles accuracy.

Recently, we have reported the first ab initio molecular dynamics determination of threshold

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displacement energies in silicon carbide [14]. In this paper, we briefly summarized the main results from these calculations, and we reported investigations on the stability of the formed Frenkel pairs for selected crystallographic directions.

Computational method

The procedure is simple: after a defined impulse is given to an atom, usually called the primary knock-on atom (PKA), the evolution of the system is monitored. Once the transferred energy exceeds E_d there is formation of a Frenkel pair. The ab initio molecular dynamics calculations were performed using the plane-wave pseudopotential code GP [15], based on the density functional theory (DFT) [16, 17]. The exchange-correlation potential proposed by Ceperley and Alder, and parameterized by Perdew and Zunger was used [18]. We considered a Γ-sampling of the Brillouin zone, and a 35 Ry kinetic cut-off. With those parameters, the calculated lattice parameter a_0=4.34 Å and the bulk modulus B=221 GPa were found to reproduce rather well experimental values, 4.36 Å and 224 GPa respectively [19]. We checked that pseudopotential cores did not overlap during simulations. Several computational issues, such as critical cell size, time step, thermostat, have also been investigated [14]. All calculations were performed with a constant number of particles, with a 64-atom cell ($2a_0$x$2a_0$x$2a_0$), except for the Si PKA in the <100> direction where a 96-atom cell ($3a_0$x$2a_0$x$2a_0$) was required to keep the PKA in the cell. A time step dt=1 a.u. was used during the ballistic phase of the simulation, and then increased to 2 a.u. during the relaxation phase. A thermostat was applied to recover the initial temperature of 300K during the latter phase. The maximum duration of each run was 2.8 ps. If a stable Frenkel pair occurred, the system was then completely relaxed to obtain the minimum energy configuration. The determination of transition configurations has been done by performing a serie of calculations where the interstitial is constrained at different positions along a recombination path.

Threshold displacement energies and related defects

We now briefly describe and discuss threshold displacement energies and associated defects in 3C-SiC, reported in Table I and Figure 1. For C[100] and an energy above 18 eV, the PKA recoils toward the nearest tetrahedral interstitial site and moves further until it forms a tilted $CC_{<100>}$ dumbbell interstitial. This configuration was previously described as the most stable *CC* dumbbell [20]. Several *CSi* dumbbells were also identified. For C[110] and E_d equal to 14 eV, the C atom replaces its C first neighbor, which is subsequently displaced to create a $CSi_{<0-10>}$. This configuration is also found in the case of a Si PKA along the <110> direction, and an energy above 45 eV, with a different collision sequence. Considering now C[-1-1-1] direction, above 16 eV, the C atom heads for the tetrahedron defined by four Si atoms, and does not form a C_{TSi} tetrahedral interstitial as it could be primarily expected, but a slightly tilted $CSi_{<010>}$ dumbbell with a Si atom. This is consistent with previous ab initio calculations from Lento *et al.*, predicting the conversion of the C_{TSi} tetrahedral interstitial to the $CSi_{<010>}$ dumbbell interstitial [21]. The last case for which a *CSi* dumbbell is obtained is the Si[-1-1-1] with E_d equal to 21 eV. Here the Si atom collides with its C first neighbor, displaces it, and returns to its original location. Silicon tetrahedral interstitials surrounded by carbon atoms Si_{TC}, which were determined as the most stable tetrahedral interstitial [20-22], were also created. The simplest case is Si[111]. Above 22 eV, the Si PKA directly moves toward the tetrahedral site and forms a Si_{TC} interstitial. A Si PKA along the <100> direction, with an energy higher than 46 eV, leads to the formation of a Si_{TC} interstitial, after a short collision sequence during which the Si PKA replaces another Si atom, which then moves in the following tetrahedral site. For the C[111] case and an energy higher than 38 eV, several mechanisms, occurring for similar energies, were observed depending on the way the C PKA rebounded on its closest silicon neighbor. In the first mechanism, the C PKA rebounds without displacing the Si atom and forms $CSi_{<100>}$, identical to C[110] and Si[110] cases. In the others, the C PKA encounters its Si first neighbor at short distance with enough energy to displace it to the next Si_{TC}

interstitial site. Afterwards, the C PKA sometimes returns to its original location, leading to a final configuration similar to the Si[111] case, or it bounces backward, and after few recombinations forms additional defects such as C_{Si} antisite and carbon vacancy V_C, as shown in Fig. 1. In this peculiar case, there is an uncertainty regarding the created defects, but for a similar E_d, a somewhat different result than in previous works [9]. Globally, our calculations show that mostly dumbbells and Si_{TC} interstitials are formed, with a vacancy-interstitial d_{FP} separations between $0.5a_0$ and $1.5a_0$, in fair agreement with the relative stability of defects found with static ab initio calculations.

Table 1: Threshold displacement energies in 3C-SiC, as well as associated defects and Frenkel pair separations d_{FP}, calculated with DFT-LDA molecular dynamics, along the main crystallographic directions. V_C, V_{Si}, CC, CSi and Si_{TC} correspond respectively to a carbon vacancy, a silicon vacancy, a carbon-carbon dumbbell, a carbon-silicon dumbbell and a silicon atom in a carbon tetrahedral site. The average values are weighted for equivalent directions. For the C[111] case, several defects were observed.

Direction	E_d (eV)	Defect	d_{FP} (a_0)
C[100]	18	$V_C + tilted\ CC_{\langle 100\rangle}$	0.87
C[110]	14	$V_C + CSi_{\langle 0\bar{1}0\rangle}$	0.48
C[111]	38	/	/
C[$\bar{1}\bar{1}\bar{1}$]	16	$V_C + CSi_{\langle 010\rangle}$	0.95
C sublattice, weighted average: 19 eV			
Si[100]	46	$V_{Si} + Si_{TC}$	1.52
Si[110]	45	$V_C + CSi_{\langle 0\bar{1}0\rangle}$	0.48
Si[111]	22	$V_{Si} + Si_{TC}$	0.87
Si[$\bar{1}\bar{1}\bar{1}$]	21	$V_C + CSi_{\langle 0\bar{1}0\rangle}$	1.24
Si sublattice, weighted average: 38 eV			

The average E_d on both C and Si sublattices, calculated by weighting each values of E_d by the number of equivalent directions [23], are reported on table I. They are in very good agreement with the values usually considered by the fusion community: 19 eV against 20 eV for the C sublattice, and 38 eV against 35 eV for the Si sublattice.

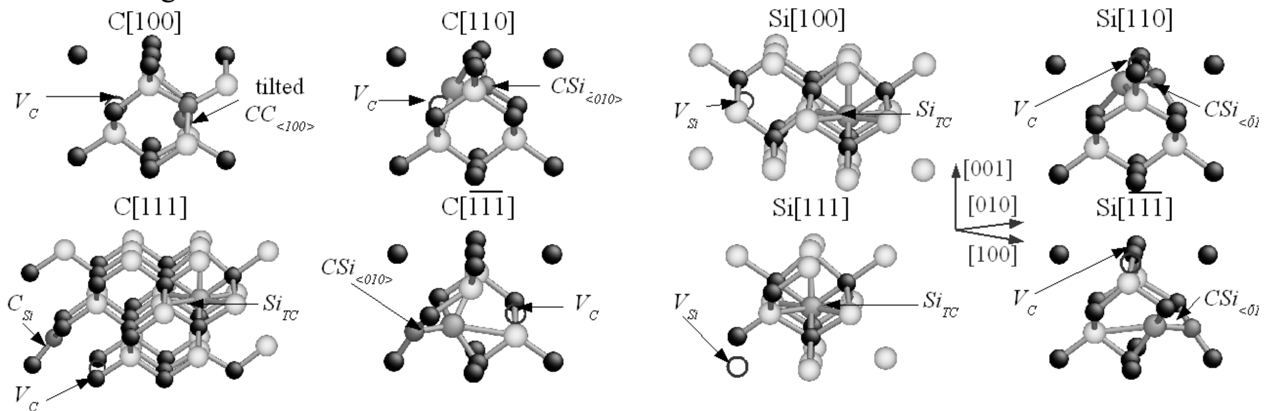

Fig. 1: Defect configurations for each considered crystallographic directions. Carbon atoms are drawn in black, and silicon atoms in light grey. Defects are drawn in grey, and the vacancies are represented by an open circle.

Stability of created Frenkel pairs

The stability of the created defects depends on the recombination energy, which is simply the difference between the energy of the Frenkel pair and the highest energy along the minimal energy recombination path (saddle point). In the framework of harmonic transition state theory[24], the lifetime τ of a Frenkel pair is given by

$$\tau=\tau_0\exp(E_a/kT), \quad (1)$$

where τ_0 is a pre-exponential factor proportional to the inverse of the Debye frequency and the activation energy E_a is the recombination energy.

With a simulation time of 2.8 ps, no recombination process was observed. Investigating the stability of Frenkel pairs with Arrhenius plot is obviously beyond the reach of ab initio molecular dynamics. It is also pointless to use empirical potentials in this case, since they are known to provide an inaccurate description of saddle points in SiC. Consequently, we decided to study the stability of Frenkel pairs by directly determining the transition states for recombination processes. Our investigations have been restricted to three cases of defects, corresponding to a C[100], a Si[100], and a Si[111] PKA, for which there are straight recombination paths. Transition states can then be easily obtained, both geometrically and energetically obtained, from constrained path calculations. Here, we focussed on direct combination mechanisms. However, it is possible that more complex mechanisms, such as two atoms exchange or concerted diffusion, play a role and significantly lower the energy recombination.

The calculated energies of formation and recombination barriers of Frenkel pairs are reported in Fig. 2. First, we found that the formation energies of Frenkel pairs are qualitatively in agreement with the formation energies of single point defects. Due to the short separation distance, there is a non negligible interaction between the interstitial and the vacancy, of the order of one eV. Second, the recombination barriers are rather high, in agreement with the observed stability of the created Frenkel pairs during the simulations. For example, assuming a pre-exponential factor equal to the inverse of the Debye frequency of 3C-SiC (4.10^{-14} s), with the lowest activation energy, 1.18 eV, corresponding to the Si[111] case (V_{Si}+Si_{TC}, d_{FP}=0.87a_0), the estimated lifetime is about 28 days at 300 K. The lifetime is still 370 ps at 1500 K. It clearly shows that such an investigation is out of the reach of ab initio molecular dynamics. Isochronal and thermal annealing experiments on irradiated 6H-SiC have suggested that activation energies for thermal recovery are estimated to be 0.3±0.15 eV between 170 and 300 K (stage I), 1.3±0.25 eV between 420 and 550 K (stage II), and 1.5±0.3 eV between 570 and 700 K (stage III) [11-12]. A similar behavior is expected for cubic silicon carbide, since the local atomic environment is similar for both hexagonal and cubic structures. For the Si[111] Frenkel pair, our value for the activation barrier is compatible with the stage II value. The other activation energies, respectively 2.55 eV and 2.83 eV for the Si[100] and C[100] Frenkel pairs, are much higher than the stage III value. For example, the temperatures needed for a lifetime of 1 min are about 840 K and 935 K, respectively. It is likely that a more complex recombination mechanism would occur, with a lower activation energy. It would be useful to use saddle point search methods, such as the dimer method [25], to investigate these other recombination processes.

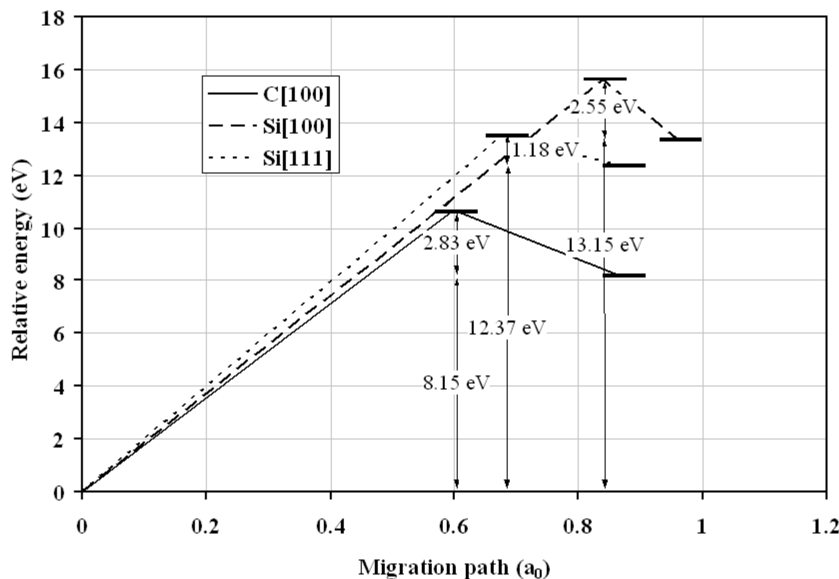

Fig. 2: Formation energies and activation barriers (in eV) for the recombination of selected Frenkel pairs. The energies of the saddle points and of the Frenkel pairs are plotted against the corresponding distance between the interstitial and the vacancy (in lattice parameter a_0).

Conclusion

Using ab initio molecular dynamics, we have determined threshold displacement energies in cubic silicon carbide. Average values were found in close agreement to the experimental consensus for both C and Si sublattices. Such an agreement, both with the experiment and the calculated defect formation energies, has not been obtained with previous classical molecular dynamics studies, and justifies the use of first principles methods for the determination of threshold displacement energies in covalent materials. We have also investigated the stability of selected created Frenkel pairs, focussing on simple recombination mechanisms. We found one activation energy in agreement with existing data available from isochronal and thermal annealing experiments on irradiated 6H-SiC.

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